

and only 253 measurements were refined by least squares. The agreement of the results is quite good with Mo—Mo approaches of 2.5296 (6) Å inside the Mo_3 clusters and 3.2436 (6) Å with the closest Mo in the neighbouring cluster for the Fe compound, as compared with 2.524 (2) and 3.235 (2) Å for the Zn compound. The average Mo—O distances are, respectively, 2.051 (2) and 2.03 (1) Å with similar distortions around the Mo atom. The distortions around the Fe^{2+} seem to be marginally larger than those around Zn^{2+} possibly because Fe^{2+} , a high-spin $3d^6$ ion, has an unsymmetrical occupation of the t_{2g} levels while Zn^{2+} has a filled $3d$ shell.

The similarity of the present calculated powder pattern of $\text{Fe}_2\text{Mo}_3\text{O}_8$ with the JCPDS pattern #19-611 raises serious doubts about the existence of the phase FeMoO_3 described by Rusakov *et al.* (1965). Such a compound has not been found in a phase study of the Fe—Mo—O system at 1413 K (Abe, 1972), although its melting point is reportedly 1853 ± 30 K. The density measured for 'FeMoO₃' agrees well with those observed and calculated for $\text{Fe}_2\text{Mo}_3\text{O}_8$ by McCarroll *et al.* (1957), respectively 6.00, 6.04 and 6.02 Mg m^{-3} . On the other hand, 5.13 formulae of FeMoO_3 would be required to explain the measured density and this value seems unlikely. In our opinion, the JCPDS pattern

#19-611 is an incorrectly indexed pattern of $\text{Fe}_2\text{Mo}_3\text{O}_8$. In the same way, the pattern #18-845 for MgMoO_3 described by the same authors should be re-examined: the pattern can be indexed using the cell parameters for $\text{Mg}_2\text{Mo}_3\text{O}_8$ and the observed densities agree (5.20 and 5.30 Mg m^{-3}).

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Structure of Sodium Hydrogenphosphate

BY R. G. HAZELL, A. C. HAZELL AND B. KRATOCHVÍL*

Department of Inorganic Chemistry, Århus University, DK-8000 Århus C, Denmark

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Abstract. $\text{Na}_{0.5}\text{H}_{2.5}\text{PO}_3$, $M_r = 92.99$, trigonal, $P\bar{3}c1$, $a = 5.908$ (2), $c = 9.554$ (4) Å, $Z = 4$, $U = 288.8$ Å³, $D_c = 2.14$, $D_m = 2.135$ Mg m^{-3} , $\mu(\text{Mo } K\alpha) = 0.767$, $\mu(\text{Ag } K\alpha) = 0.392$ mm^{-1} . $R = 0.022$ ($R_w = 0.033$) for 843 reflexions [$I > 3\sigma(I)$] measured with Ag $K\alpha$ radiation, $R = 0.022$ ($R_w = 0.044$) for 884 reflexions [$I > 3\sigma(I)$] measured with Mo $K\alpha$ radiation, 23 parameters were refined. Each P tetrahedron is connected to three other P tetrahedra by hydrogen bonds so that infinite sheets of composition $[\text{H}_{2.5}\text{PO}_3]_n^{(n/2)-}$ are formed in the structure parallel to the xy plane. The sheets are held together by the Na^+ ions.

Introduction. The study of the title compound was undertaken as part of an investigation of the $\text{Na}_2\text{HPO}_3\text{—H}_3\text{PO}_3\text{—H}_2\text{O}$ system. The compound $\text{NaH}_2\text{PO}_3\text{·H}_3\text{PO}_3$ was first described by Lefforge & Hudson (1952) and Ebert & Škvára (1964) found the exact conditions for its crystallization.

A crystal of dimensions $0.45 \times 0.45 \times 0.75$ mm sealed in a glass capillary was mounted on a Picker FACS-1 diffractometer. Cell dimensions were calculated from the setting angles of 15 reflexions measured at $\pm 2\theta$ using Mo $K\alpha$ radiation. Reflexions were measured out to $2\theta = 100^\circ$ with Zr-filtered Mo $K\alpha$ radiation. A second data set ($2\theta_{\text{max}} = 80^\circ$) was collected with Pd-filtered Ag $K\alpha$ radiation. In both cases an $\omega\text{—}2\theta$ scan was used with a step length of 0.04° and a counting time of 1 s step^{-1} . The scan widths were $(3.0 + 0.692 \tan \theta)^\circ$ for Mo $K\alpha$ radiation

* Present address: Department of Inorganic Chemistry, Charles University, Albertov 2030, 128 40 Praha 2, Czechoslovakia.

and $(3.0 + 0.9 \tan \theta)^\circ$ for Ag $K\alpha$ radiation. The data were corrected for absorption. The structure was determined from the Mo $K\alpha$ data by means of Patterson and Fourier syntheses. H-atom positions were obtained from a difference map.

Attempts at least-squares refinement were not successful. In particular the atom H(2) always moved too close to the O atom giving O—H of about 0.5 Å. The data suffered badly from extinction; also the crystal was mounted with c parallel to the φ axis of the diffractometer so that there was a large probability of errors from double reflexion. Consequently, a new data set was collected with Ag radiation to reduce errors from extinction and absorption. To reduce the possibility of double reflexion c was turned 7° away from the φ axis.

Refinement with the Ag data still gave a short O—H distance unless the low-order reflexions were omitted from the refinement. The extinction correction undercorrected for strong reflexions in the $hk0$ plane and overcorrected for those along the $00l$ axis. Refinement with anisotropic extinction (Thornley & Nelmes, 1974) gave a final R value of 0.022* ($R_w = 0.033$) for 843 reflexions with $F_o^2 > 3\sigma(F_o^2)$. H(2) also refined to a position which made sense chemically. As there was good agreement between symmetry-related reflexions, we constrained the extinction parameters to be uniaxial with the unique axis parallel to c . The extinction parameters obtained were $g_{11} = 0.64(7) \times 10^{-4}$ and $g_{33} = 0.15(1) \times 10^{-4}$ corresponding to a minimum F_o^2/F_o^2 (corr.) of 0.32.

We then tried refining using the Mo data assuming anisotropic extinction and obtained a final R value of

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36543 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^5$ for P, Na and O, $\times 10^3$ for H) and isotropic thermal parameters ($\text{Å}^2 \times 10^{-4}$)

For non-H atoms, $U_{iso} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$. The values determined from the data collected with Ag radiation are given first.

	x	y	z	U_{iso}
P	66667	33333	59647 (2)	152 (1)
	66667	33333	59640 (3)	157 (1)
Na	0	0	0	251 (3)
	0	0	0	255 (3)
O	38808 (8)	25506 (11)	64044 (5)	234 (2)
	38801 (9)	25546 (11)	64008 (6)	242 (2)
H(1)	667	333	465 (1)	75 (32)
	667	333	468 (6)	227 (63)
H(2)	389 (4)	341 (4)	710 (2)	329 (64)
	390 (7)	335 (10)	678 (4)	705 (114)

0.22 ($R_w = 0.044$) for 884 reflexions with $F_o^2 > 3\sigma(F_o^2)$. The extinction parameters were $g_{11} = 0.22(2) \times 10^{-4}$ and $g_{33} = 0.024(2) \times 10^{-4}$ corresponding to a minimum F_o^2/F_o^2 (corr.) of 0.19. Although this refinement gave an R as low as that obtained with the Ag data, the H-atom positions were less accurate and an unreasonably short O—H(2) distance was obtained. Coordinates and thermal parameters from the two refinements are almost identical. The largest discrepancies are for the H atoms, especially for H(2) which has an occupation factor of 0.5. In the Discussion the results of the refinement with Ag $K\alpha$ data are used since the data suffered least from systematic errors and gave the lowest weighted R values. The weighting scheme used was $w = \{[\sigma(F_o^2) + 1.02 F_o^2]^{1/2} - |F_o|\}^{-2}$. Scattering factors were those of Cromer & Mann (1968) for Na, P and O, and of Stewart, Davidson & Simpson (1965) for H. The final fractional coordinates are given in Table 1.

Calculations were carried out on a Cyber 173 computer with the following programs: PROFILE, DATAP and DSORTH (State University of New York at Buffalo) — data reduction, including absorption correction; ZALKINS (A. Zalkin, Lawrence Radiation Laboratory) — Fourier synthesis; LINUS (Coppens & Hamilton, 1970) — least-squares refinement; ORFFE (Busing, Martin & Levy, 1964) — calculation of molecular geometry; ORTEP (Johnson, 1965) — drawings.

Discussion. The structure is drawn in Fig. 1 and the interatomic distances and angles are given in Table 2. The P atom is tetrahedrally coordinated by three O atoms and by H(1). Each P tetrahedron is connected to three other P tetrahedra by strong O...H(2)...O bonds so that infinite sheets of a composition $[\text{H}_{2.5}\text{PO}_3]_n^{(n/2)-}$ are formed in the structure parallel to the xy plane. Hydrogen bonds are present only within the sheets. For H(2) the difference synthesis had two well-resolved maxima related by a twofold axis. In potassium hydrogen tartrate, Kroon & Kanters (1972) found a double maximum with H—H = 0.8 and O—O = 2.48 Å from an X-ray study at 113 K. Currie, Speakman, Kanters & Kroon (1975) in a neutron diffraction study of potassium hydrogen tartrate found a much smaller separation of the H sites. They concluded that double maxima are not necessarily valid evidence for a disordered hydrogen bond and that the X-ray result is anomalous and may be connected with the asphericity effect (Macdonald, Speakman & Hadži, 1972; Coppens & Coulson, 1967). Our results are similar to the X-ray results of Kroon & Kanters (1972), but they also show the apparent H—H distance to be very sensitive to experimental errors such as extinction. The P—O distance is in the range of P—O and P—OH distances found in other phosphites (Philippot & Lindqvist, 1970; Brodalla, Goeters, Kniep, Mootz &

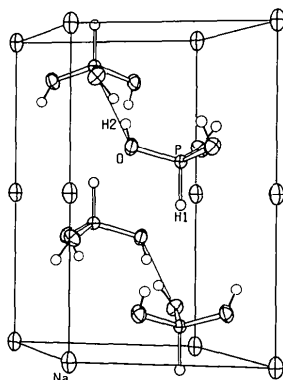


Fig. 1. Perspective view of the unit-cell contents.

Table 2. Interatomic distances (Å) and angles (°) from refinements with Ag K α and Mo K α radiations

The values in square brackets are bond distances corrected for thermal motion assuming riding motion (Busing & Levy, 1964).

Symmetry code: (i) $y, x, \frac{1}{2} - z$; (ii) $1 - y, x - y, z$; (iii) $y, x, \frac{1}{2} - z$; (iv) $-x, -x + y, \frac{1}{2} - z$.

	Ag K α	Mo K α		Ag K α	Mo K α
P—O	1.5291 (4)	1.5293 (5)	P—H(1)	1.26 (1)	1.23 (3)
	[1.5372]	[1.5375]	O—H(2)	0.84 (2)	0.59 (5)
Na—O ^{III}	2.4234 (5)	2.4216 (5)	O ^I —H(2)	1.72 (2)	2.00 (4)
O—O ^I	2.4971 (10)	2.5002 (11)	H(2)—H(2')	0.90 (4)	1.49 (8)
O—P—O ^{II}	112.76 (2)	112.85 (2)	P—O—H(2)	111 (1)	110 (4)
O ^{III} —Na—O ^I	92.30 (2)	92.40 (2)	O—H(2)—O ^I	154 (2)	144 (5)
O—P—H(1)	105.95 (2)	105.83 (2)	H(2)—O—P	119 (1)	118 (1)

Wunderlich, 1978; Loub & Paulus, 1981). According to the rigid-bond postulate (Hirshfeld, 1976), the thermal motions of the P and O atoms along the P—O bond should be the same. They do, however, differ by an amount corresponding to a possible disorder between two O sites 0.045 (2) Å apart, which is close to the difference observed between P—O and P—OH distances. An ordered structure in a space group without the twofold axes, $P3c1$, is unlikely since it would mean one P atom having three OH groups attached.

The asphericity effect may also be responsible for the short P—H(1) bond [1.26 (1) Å]. For LiH_2PO_3 a P—H distance of 1.17 (6) Å was found by X-rays (Philipot & Lindqvist, 1970), 1.396 (4) Å by neutrons (Johansson & Lindqvist, 1976). The phosphite sheets

are held together by the Na^+ ions which have six O neighbours in an octahedral arrangement. Since all P atoms are equivalent in the structure it seems more correct to prefer a formula unit of $\text{Na}_{0.5}\text{H}_{2.5}\text{PO}_3$ to $\text{NaH}_2\text{PO}_3 \cdot \text{H}_3\text{PO}_3$ for the compound studied.

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